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Software package to calculate the effects of the core hole and surface excitations on XPS and AES†

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We report on a new software package that allows to calculate the energy loss processes in a photo- and Auger electron spectrum. The calculations are performed within our previously published semiclassical dielectric response model. The model takes into account energy loss, which takes place because of the sudden creation of the static core hole and as the photoelectron travels in the bulk, passes the surface region and continues in the vacuum where it interacts with its image charge before it ends up in the electron spectrometer. It is a one-step model, which includes interference effects between these excitations. The only input in the calculations is the dielectric function of the material. We discuss the capabilities of the software and illustrate some examples of its practical application, including comparison with experimental spectra. We hope the software will be useful for the investigations of fundamental excitation mechanisms in XPS and AES. The software is free for noncommercial use. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: XPS; intrinsic; extrinsic; core hole; surface excitation; quantitative

Introduction

The quantitative interpretation of photoelectron spectra requires models to describe the energy loss processes that are responsible for the energy distribution in the measured energy spectra of emitted photoelectrons. These are often divided into three processes: photoexcitation process (which includes the effect of the core hole), transport to the surface region (energy loss in the bulk) and passage through the surface and vacuum region to the electron energy analyser (energy loss in the surface region and while the electron travels in the vacuum). For an accurate description, it turns out that these three effects cannot be treated as separate contributions because they interfere, and an accurate description requires a one-step description rather than a division into three separate effects. This has been known for more than 30 years, where model calculations of energy loss in XPS were performed from first-principles quantum-mechanical descriptions.[1–4] These models have been extremely valuable to enlighten the fundamental mechanisms behind the photoexcitation process. However, the complexity of this approach makes it impractical for calculations other than for the free-electron-like solids.

To obtain a more practical and manageable model for XPS, we proposed a semiclassical dielectric response model[5,6] in which the interaction between the time-varying electric fields from the charges (i.e. the moving photoelectron and the static core hole) and the electronic states of the solid, with the boundary conditions imposed by the surface, are described by the dielectric function of the material. This is a one-step model where the effects along the full trajectory from the point of excitation in the solid to the electron spectrometer are calculated and thus it includes contributions from interference effects. With this model, extensions beyond the nearly free-electron-like materials are straightforward because the only input in the calculations is the dielectric function of the material.

Within this semiclassical model, there are two origins to the energy loss structure. The first is due to the sudden creation of an electric field from the core hole, which appears because of photoexcitation of the core electron. This field excites valence electrons, and the excitation energy is lost by the photoelectron. The second contribution is due to the time- and space-varying electric field from the moving photoelectron, which also cause excitations, and thereby energy loss and such processes occur even after the photoelectron has left the surface because of the interaction of the photoelectron with its image charge. The energy loss processes corresponding to these two contributions are usually called *intrinsic* and *extrinsic* excitations, respectively, although a strict separation is not possible because the effects interfere as mentioned earlier.

We have previously presented a similar semiclassical one-step model for the quantitative interpretation of the energy loss observed in reflection electron energy loss spectroscopy (REELS).[7–9] This model was found to quantitatively account well for the observed changes in energy loss structure for a wide range of geometries and for energies down to at least 200 eV.[8,10] It was also found that the REELS spectra cannot be interpreted as a simple linear combination of a bulk and a surface excitation term. The reason for this is that there is an interference

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between surface and bulk excitations, which causes the shape of the loss structure to vary with the depth the individual electron has reached before it is backscattered.[8,11] A software package QUEELS–$\varepsilon(k,\omega)$–REELS was developed,[9] which allows to apply this theory to determine the complex dielectric function $\varepsilon(k,\omega)$ from analysis of a REELS spectrum. This REELS software has been widely used to determine the dielectric function for several materials as well as for nanometer thin films.[12–15]

Because this semiclassical REELS model has proven to give a good description of the energy loss processes, one might expect the corresponding semiclassical dielectric response model for XPS also to be quite accurate. The main difference is that in XPS, there is a static core hole, which is created simultaneously with the photoelectron. So far, the semiclassical XPS model has, for example, been used to calculate XPS spectra from different materials,[5–7,16–18] and good agreement with experimental spectra was found. It was also successful in similar calculations of the effect in AES,[17] where two core holes are present. Recently, it was used to calculate the combined effects of core hole and surface excitations[19] on measured XPS peak intensities.

Although the only input in the model is the dielectric function, the theory and the corresponding equations are rather complex, and this has been a hindrance for other groups to apply the model. To make the model available for practical use by other groups, we have therefore developed a user-friendly software package called Quantitative Analysis of Electron Energy Loss in XPS (QUEELS-XPS).

The model

In the semiclassical model[5,6] based on a dielectric response description, it is assumed that an electron–hole pair (both considered as point charges) is created at a given depth inside a semi-infinite medium, characterised by a dielectric function $\varepsilon(k,\omega)$. The calculation applies the 'specular reflection model',[20] which allows one to solve the electrodynamic problem with the proper boundary conditions for the electric potential and field at the surface–vacuum interface. The geometry of the situation is defined in the inset of Fig. 1. The core hole is assumed to be static

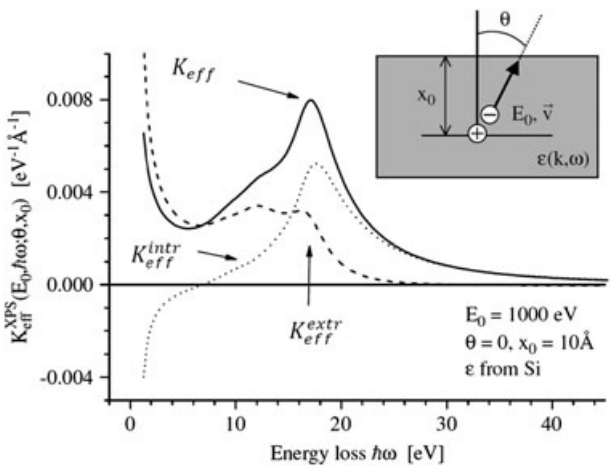

Figure 1. Effective inelastic scattering cross section for Si2p photoemission at a 10-Å depth in Si. The Si2p core electron has been photoexcited to 1000 eV kinetic energy. The contribution to the losses induced by the core hole (intrinsic) has been isolated from losses caused by transport of the photoelectron (extrinsic). From Tougaard and Yubero.[7]

with infinite lifetime, that is, it remains at a fixed location forever after being created at time $t = 0$. The photoelectron escapes from the semi-infinite medium with a velocity v in a rectilinear trajectory. Within this model, one defines an effective inelastic scattering cross section $K_{\text{eff}}(E_0,\hbar\omega;\varepsilon,\theta,x_0)$ in terms of the induced potential. $K_{\text{eff}}(E_0,\hbar\omega;\varepsilon,\theta,x_0)$ is defined as the average probability that a photoelectron excited at depth x_0 with energy E_0 shall lose energy $\hbar\omega$ per unit energy loss and per unit path length while travelling in the specified geometry. The energy loss includes processes that take place after the electron has left the surface, but the average is taken over the path length travelled inside the solid, that is, $x = x_0/\cos\theta$, where θ is the angle to the surface normal. Neglecting angular electron deflection one gets[5]

$$K_{\text{eff}}(E_0,\hbar\omega;\varepsilon,\theta,x_0) = \frac{2}{(2\pi)^4\hbar^2\omega x_0} \Re e\left\{ \int dt \int d^3r\, \rho_e(r,t) i \int d^3k\, k\cdot v\, \Phi_{\text{ind}}(k,\omega;\varepsilon,\theta,x_0) e^{i(kr-\omega t)} \right\} \quad (1)$$

where r is the position, $\rho_e(r,t)$ is the charge density of the escaping photoelectron and $\Phi_{\text{ind}}(k,\omega;\varepsilon,\theta,x_0)$ is the Fourier transform of the potential induced by the escaping photoelectron and the static core hole in the semi-infinite medium.

The final expression for $\Phi_{\text{ind}}(k,\omega;\varepsilon,\theta,x_0)$, given by Cohen Simonsen *et al.*[5], has several terms that, from their dependence on the charge of the static hole, can formally be identified as being due to the static core hole (denoted 'hole' terms) and the rest, which are independent of the hole (denoted 'no-hole' terms) so that

$$\Phi_{\text{ind}}(k,\omega;\varepsilon,\theta,x_0) = \Phi_{\text{ind,no-hole}}(k,\omega;\varepsilon,\theta,x_0) + \Phi_{\text{ind,hole}}(k,\omega;\varepsilon,\theta,x_0) \quad (2)$$

This is a formal division, and it is not strictly possible to make this distinction because the different contributions interfere. More details and the precise expressions for the 'no-hole' and 'hole' contribution to the total induced potential can be found in the work of Cohen Simonsen *et al.*[5] The equations are quite involved and will not be repeated here. It is common to denote those excitations that are due to the potential $\Phi_{\text{ind,hole}}$ as 'intrinsic' and those that are due to the potential $\Phi_{\text{ind,no-hole}}$ as 'extrinsic'. With this identification, the total cross section is decomposed in the form

$$K_{\text{eff}}(E_0,\hbar\omega;\varepsilon,\theta,x_0) = K_{\text{eff}}^{\text{extr}}(E_0,\hbar\omega;\varepsilon,\theta,x_0) + K_{\text{eff}}^{\text{intr}}(E_0,\hbar\omega;\varepsilon,\theta,x_0) \quad (3)$$

where $K_{\text{eff}}^{\text{intr}}(E_0,\hbar\omega;\varepsilon,\theta,x_0)$ is the sum of the terms that would disappear from the equations if the core hole was not present and $K_{\text{eff}}^{\text{extr}}(E_0,\hbar\omega;\varepsilon,\theta,x_0)$ is the sum of the remaining terms. Note that with this separation in 'intrinsic' and 'extrinsic' excitations, the terms include the so-called 'interference' effects that may be attributed to the interference between the fields from the core hole and the moving electron. Because the interference effect diminishes the total energy loss, the intrinsic cross section may be negative (see Fig. 1). However, the real total cross section K_{eff} is always positive.

In an experimental XPS measurement, there will be contributions from photoelectrons excited at a range of depths. It is therefore necessary to account for their relative contributions to the spectrum. This is performed by introducing an averaged effective cross section[5,6]

$$K_{\mathrm{eff,av}}(E_0,\hbar\omega;\varepsilon,\theta) = K_{\mathrm{eff,av}}^{\mathrm{extrinsic}}(E_0,\hbar\omega;\varepsilon,\theta) + K_{\mathrm{eff,av}}^{\mathrm{intrinsic}}(E_0,\hbar\omega;\varepsilon,\theta) \quad (4)$$

where the 'extrinsic' and 'intrinsic' contributions can be estimated as weighted averages over the total path length x travelled by the electron inside the medium as

$$K_{\mathrm{eff,av}}^{\mathrm{extrinsic/intrinsic}}(E_0,\hbar\omega;\varepsilon,\theta) = \int_0^\infty W(E_0;\varepsilon,\theta,\mathrm{a})K_{\mathrm{eff}}^{\mathrm{extrinsic/intrinsic}}(E_0,\hbar\omega;\varepsilon,\theta,\mathrm{a})\mathrm{d}x \quad (5)$$

The weight function $W(E_0;\varepsilon,\theta,a)$ takes into account the path-length distribution of the electrons having suffered only a single inelastic scattering event. For a homogeneous solid, it is given by[6]

$$W(E_0;\varepsilon,\theta,a) = \frac{a\cdot\exp[-a/\lambda_{\mathrm{eff}}(E_0;\varepsilon,\theta,a)]}{\int_0^\infty x\cdot\exp[-x/\lambda_{\mathrm{eff}}(E_0;\varepsilon,\theta,a)]\mathrm{d}x} \quad (6)$$

where $\lambda_{\mathrm{eff}}(E_0;\varepsilon,\theta,a)$ is the inverse of the area of the corresponding cross section $K_{\mathrm{eff}}(E_0,\hbar\omega;\varepsilon,\theta,a)$

$$\lambda_{\mathrm{eff}}(E_0;\varepsilon,\theta,a) = \left[\int_0^\infty K_{\mathrm{eff}}(E_0,\hbar\omega;\varepsilon,\theta,a)\mathrm{d}\hbar\omega\right]^{-1} \quad (7)$$

$\lambda_{\mathrm{eff}}(E_0;\varepsilon,\theta,a)$ is thus the inelastic mean free path for an electron starting at depth a towards the surface in direction θ travelling in a material described by the dielectric function ε. Note that $\lambda_{\mathrm{eff}}(E_0;\varepsilon,\theta,a)$, besides the well-known dependence on the dielectric properties of the material, depends on both a and θ. This result is a consequence of surface excitations as well as excitations that take place in the vacuum after the electron has left the surface.

It should be noted that this model, of course, does not include any effects that are part of the initial photoexcitation process. It only evaluates those energy loss processes, which are due to the static core hole, the moving photoelectron and the surface. It is also assumed that the core hole and photoelectron are point charges whereas in reality they may be in delocalised states.

The software

The user interface of the software is shown in Fig. 2. The calculation consists of three steps as seen by the menu buttons in the centre of Fig. 2. Selecting one of these menus leads to a new screen in which the settings for the calculations are defined. The first step is 'Set ELF oscillators'. Here, the dielectric function of the material is specified in terms of j oscillators:

$$\mathrm{Im}\left(-\frac{1}{\varepsilon(k,\hbar\omega)}\right) = \theta(\hbar\omega - E_g)\cdot\sum_{i=1}^{j}\frac{A_i\gamma_i\hbar\omega}{\left[\left(\hbar\omega_{0i} + \alpha_i\frac{\hbar^2k^2}{2m}\right)^2 - \hbar^2\omega^2\right]^2 + (\gamma_i\hbar\omega)^2} \quad (8)$$

where A_i, γ_i and $\hbar\omega_{0i}$ are the strength, width and energy position of the ith oscillator. The dispersion for each oscillator is given by α_i. These parameters can, for example, be determined by analysis of a REELS spectrum,[8–15] or they may be taken from optical data.[21] For valence electrons in metals, $\alpha_i \sim 1$ whereas $\alpha_i \sim 0$ is typically found for core electrons and for valence electrons in wide-gap insulators like SiO_2 and ZrO_2;[12,13] the latter is expected because of the weak k-dispersion for the corresponding electron energy bands. For valence–electron excitation in Si, which has a smaller band gap, $\alpha_i \sim 0.5$ is found.[12] The step function $\theta(\hbar\omega - E_g)$ is included to handle the effect of a possible energy gap E_g because no energy loss process is possible for $\hbar\omega < E_g$.

After the dielectric function has been set, the next step is to calculate the cross sections $K_{\mathrm{eff}}(E_0,\hbar\omega;\varepsilon,\theta,x_0)$ (Eqn (1)). This is performed in the menu 'Calculate set of cross sections'. In this step, the geometry given by the emission angle θ and the kinetic energy E_0 of the photoelectron are set. It is also possible to set the value of the core hole charge to simulate the conditions in, for example, AES where two core holes are created. After this, the software calculates $K_{\mathrm{eff}}(E_0,\hbar\omega;\varepsilon,\theta,x_0)$ for 65 depths x_0 where the photoelectrons are created. These depths are selected automatically by the software to give a representative distribution over the relevant depths. The software first calculates the inelastic mean free path (λ) of the electron, and from this it calculates a distribution of depths, with a denser grid for small x_0 where the change in $K_{\mathrm{eff}}(E_0,\hbar\omega;\varepsilon,\theta,x_0)$ is largest. This set of 65 cross sections $K_{\mathrm{eff}}(E_0,\hbar\omega;\varepsilon,\theta,x_0)$ is stored in a matrix. The separate contributions $K_{\mathrm{eff}}^{\mathrm{intr}}(E_0,\hbar\omega;\varepsilon,\theta,x_0)$ and $K_{\mathrm{eff}}^{\mathrm{extr}}(E_0,\hbar\omega;\varepsilon,\theta,x_0)$ (Eqn (3)) of intrinsic and extrinsic contributions to the cross section are stored in separate matrices. The software allows to show and save the individual contributions for each x_0.

Figure 1 shows an example of such a calculation[7] of XPS for photoexcitation of a Si core electron to 1000 eV energy in Si at depth $x_0 = 10$ Å and normal emission. Note that less than half of the bulk plasmon intensity (at ~16 eV energy loss) is caused by the extrinsic processes occurring as the electron is transported from a 10-Å depth and out of the solid while the major part of the bulk plasmon intensity is intrinsic, that is, caused by the static core hole. It is also seen that the intrinsic plasmon is asymmetric towards higher energy loss, whereas the extrinsic plasmon is essentially symmetric. This is more clear in the work of Yubero and Tougaard,[6] where the variations in surface and bulk excitations and their individual contributions from extrinsic and intrinsic excitations were studied in detail as a function of emission angle. Such comprehensive investigations are easily performed with the software.

In an experimental XPS measurement, there will be contributions from photoelectrons excited over a range of depths, and it is necessary to account for their relative contributions to the spectrum. This step is performed in the menu 'Calculate averaged cross section $K_{\mathrm{eff,av}}$ for XPS', where K_{eff} is calculated according to Eqns (4) and (5). To be self-consistent with the calculated $K_{\mathrm{eff,av}}$, λ is taken as the inverse of the area of $K_{\mathrm{eff,av}}$, although the software also allows to input another value for λ. The software allows to calculate $K_{\mathrm{eff,\,av}}$ for a semi-infinite material as well as from a slab of a given thickness.

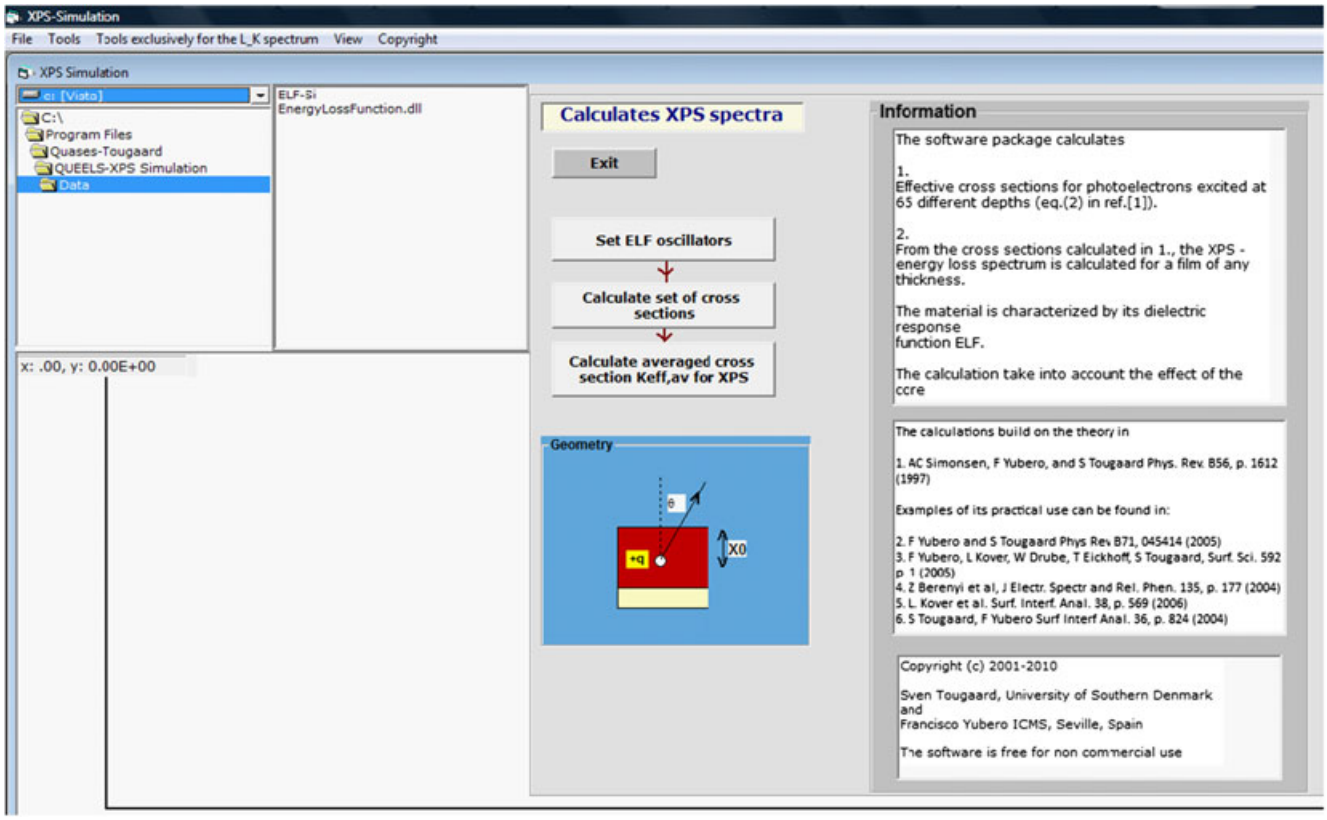

Figure 2. Main user interface to the QUEELS-XPS software.

For direct comparison with photoemission experiments, the elastic peak must be included. If $F(E)$ is the primary excitation spectrum, the model spectrum $J(E)$ from a homogeneous sample corresponding to one inelastic scattering event is given by

$$J(E) \propto F(E) + \lambda \int_{E}^{\infty} F(E')K_{eff,av}(E_0, E' - E)dE' \qquad (9)$$

where $E'-E = \hbar\omega$. $J(E)$ represents the model XPS spectrum corresponding to a zero-loss peak $F(E)$ together with the single inelastic scattering contribution. In practice, $F(E)$ can be taken as a mixed Gaussian–Lorentzian curve with a width given by the lifetime broadening of the excitation.[6]

The validity of the dielectric model for simulation of XPS spectral line shapes has been investigated by comparison with experiments.[5,6,16–18] For example, in the work of Yubero and Tougaard,[6] it was shown that the theory accounts well for the peak shapes observed in experiments for the angular dependence of Al2s and Al2p emission. The comparison is shown in Fig. 3, where the bulk and surface plasmons (at ~15 and 10 eV, respectively) are clearly

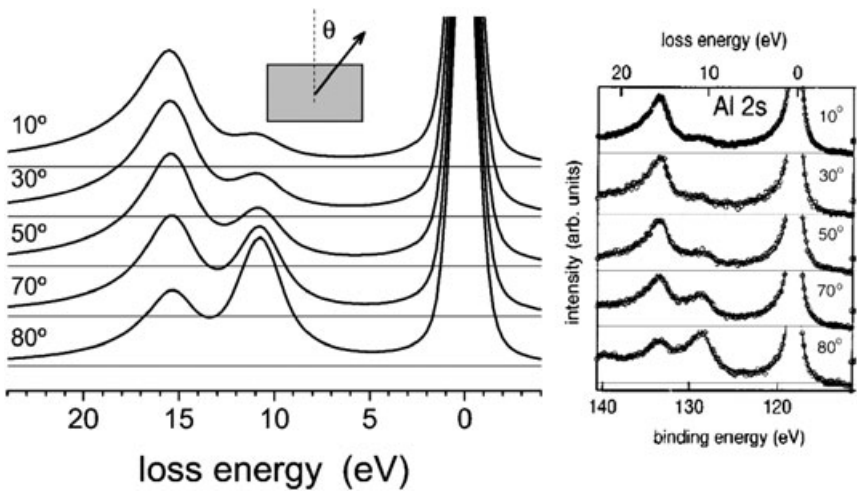

Figure 3. Left: model photoemission spectra calculated according to Eqn (9) for Al2s photoelectrons travelling in Al with 1130 eV kinetic energy for several emission angles. Right: experimental results for Al2s photoemission in an Al sample from for the same experimental conditions used in the model calculations. From Tougaard and Yubero.[6]

seen to depend strongly on the geometry, with the surface plasmon being more prominent for glancing emission angles. The model calculations reproduce the absolute intensities as well as shapes of both bulk and surface excitations for the entire series of experimental spectra taken at exit angles from 10° to 80°. The only fitting parameter in this model is the width of the elastic peak.

The software calculations can easily be applied to other materials and experimental conditions. The only input in the calculations is the dielectric function, which for a given solid may be taken from compilations.[21] The dielectric functions can also be determined experimentally from a fairly simple analysis of REELS spectra using the dielectric response model and accompanying software developed for this purpose.[7–9] The QUEELS-XPS software was recently applied to study the variation in XPS peak shapes of Cu2p and Fe2p peaks from the corresponding solids with emission angle, and good agreement with experiments was found.[18]

Eqn (7) only includes single scattered electrons. This is also seen in the simulated spectra in Fig. 3, where the intensity beyond 20 eV loss is smaller than observed in the experiment. Multiply scattered electrons may be estimated by adding a term $J^{\text{mult}}(E) \propto J(E) + \sum_{n=2}^{\infty} J_n$, where J_2 represents the double-scattering contribution, J_3 represents the triple-scattering contribution, and so on. To calculate these, one may use $K_{\text{eff,av}}$, although this is strictly not the exact cross section experienced by the multiple-scattered electrons because it includes the effect of the core hole. This approach was used by Yubero and Tougaard.[18]

As was noted earlier, the model does not include any effects that are part of the initial photoexcitation process. However, these effects may be determined by comparison with the experiment. Thus, the software evaluates those energy loss processes that are due to the static core hole, the moving photoelectron and the surface. The remaining photoexcitation processes are included in the $F(E)$ function, which can be determined by comparing to experiments using Eqn (9).

Finally, we note that the software was also used recently to investigate general properties of the effect of the core hole and the surface on measured XPS peak intensities.[19]

Conclusion

We have presented a software tool to calculate the effects of the core hole and the surface on energy loss processes in photoelectron spectra. The software builds on our previously published semiclassical dielectric response model, where the interactions between the photoelectron and the core hole, the surface, and the valence electrons are described by the dielectric function of the material. It is hoped that the software will be useful in investigations of the fundamental processes in photoelectron spectroscopy. The software is free for noncommercial use.

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